

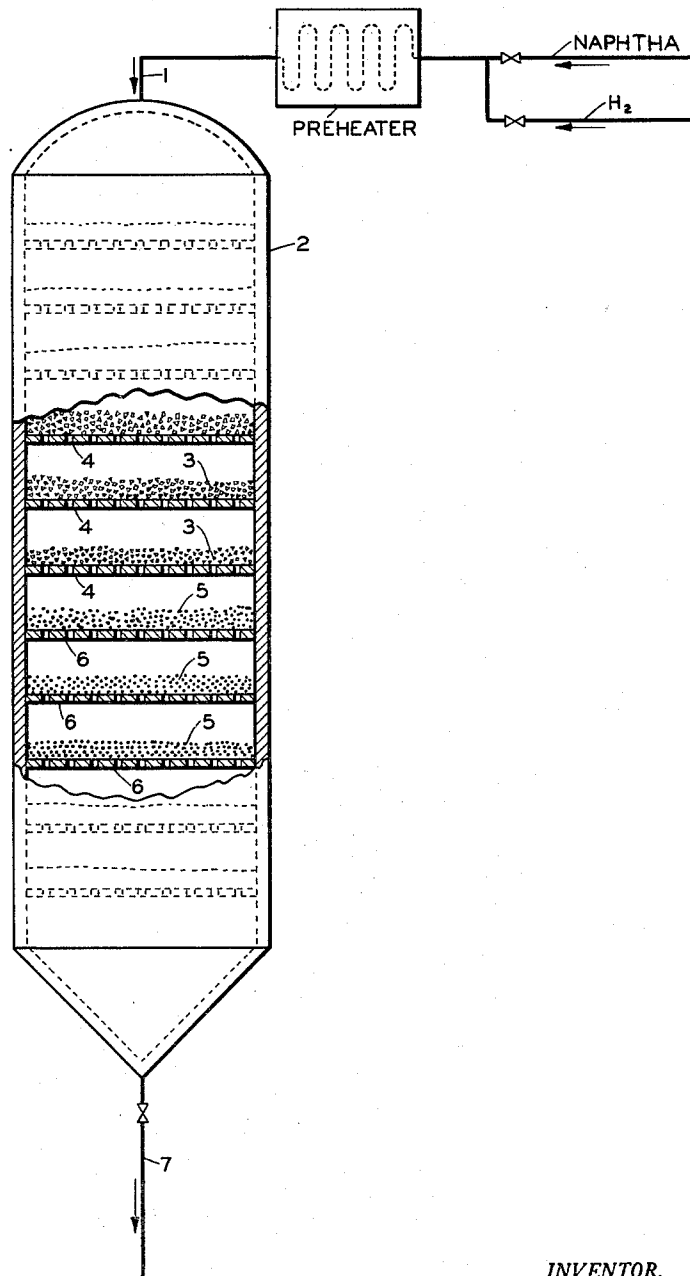
July 14, 1953

A. CLARK

2,645,604

TANDEM-BED HYDROFORMING PROCESS

Filed Sept. 7, 1949



INVENTOR.
ALFRED CLARK

BY

Hudson and Young
ATTORNEYS

UNITED STATES PATENT OFFICE

2,645,604

TANDEM-BED HYDROFORMING PROCESS

Alfred Clark, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

Application September 7, 1949, Serial No. 114,363

2 Claims. (Cl. 196—49)

1

This invention relates to the conversion of a low octane number hydrocarbon into a high octane number motor fuel component by a process of hydroforming. Hydroforming is a term applied quite generally in the petroleum conversion art and consists essentially of contacting hydrocarbons, particularly those boiling substantially in the gasoline range, with a hydroforming catalyst at a temperature of, say, 850–1150° F., a pressure of say, 50–500 pounds per square inch gauge, a feed rate of liquid hydrocarbon of about 0.2 to about 2 volumes per volume of catalyst per hour, hydrogen being added to the feed at a rate of say, 500–5000 cubic feet per barrel of naphtha. The feed streams are preheated to the initial conversion temperature. No direct heating of the catalyst is employed and, because the conversion is endothermic, the temperature of the hydrocarbons decreases during their passage through the converter. After an extended period of operation the catalyst activity decreases due to coke lay-down which then must be burned off to restore the catalyst to substantially its original activity. Among the catalysts which have been employed as hydroforming catalysts are chromia-alumina and molybdenum oxide-alumina.

In one of its embodiments this invention is concerned with a modified hydroforming process in which two catalyst stages are employed as set forth below.

1. It is known in the art that a naphtha can be treated to improve its octane number by subjecting said naphtha to hydroforming, that is, a process involving principally, dehydrogenation, cyclization and dehydroisomerization at an elevated temperature, say, in the range of 800–1050° F., under a pressure, in presence of hydrogen, say, in the range of 50–500 pounds per square inch gauge in presence of a catalyst consisting of chromia-alumina, in a first stage and of molybdenum oxide-alumina in a second stage. The effluent from the first stage is fractionated and the fraction boiling in the fairly narrow range 227–232° F. and consisting of about 90% toluene is reheated and then passed to the second stage which is to be maintained at a higher pressure than that employed in the first stage.

2. It is also known in the art to hydroform a mixture of virgin and cracked naphthas in a two-stage process with intermediate reheating of the effluent from the first stage to about 1000° F. before it enters the second stage. The catalysts disclosed include molybdenum oxide-alumina and chromia-alumina. From this prior art disclosure it appears that these catalysts can be employed in both stages of the process.

3. Still further, it has been proposed in the prior art to effect a two-stage hydroforming with a molybdenum oxide-alumina catalyst in a first stage and with a chromia-alumina cata-

2

lyst in a second stage with intermediate separation of product by solvent extraction between the two stages with reheating and treatment in the second stage of only the raffinate.

5 Since, in the process set out at (1) above, only a 90% toluene stream is passed to the second stage, it is evident to the present inventor that a highly desirable isomerization of paraffins cannot be accomplished in the said second stage.

10 Furthermore, the said process, set out at (1) hereof, has the disadvantages that intermediate cooling, fractionation, reheating, and increased pressure in the second zone as well as the attendant equipment and concomitant expense are required.

15 In the process set out at (2) above, the intermediate reheating of the first stage effluent to a temperature of about 1000° F., is considered by the present inventor to be too high to effect an optimum paraffin isomerization in the second stage in presence of molybdenum oxide-alumina. Also, said process, set out at (2) hereof, requires highly specific charge stocks but, evidently, does not teach that any combination and order of the catalysts disclosed shall be employed. Furthermore, there is involved the intermediate reheating which, as stated, is considered to be a disadvantage from both optimum operation and expense viewpoints.

20 The process set forth at (3) above teaches an order of catalysts opposite to that of the process set forth at (1) hereof. Also, the said process set forth at (3) above requires intermediate solvent extraction and reheating steps.

25 From the foregoing presentation of three prior art processes in which at least one of the hydroforming reactions appears to be effected it is evident that a simplified operation would be highly desirable.

30 It is among the objects of this invention to provide a simplified process for the hydroforming of a hydrocarbon.

35 Also among the objects of this invention is to provide a two-stage hydroforming process in which the octane number of a hydrocarbon is materially increased, without necessity of intermediate product separation by fractionation or solvent extraction.

40 Further among the objects of this invention is to provide a two-stage hydroforming process which does not require reheating of the hydrocarbon effluent from the first stage.

45 Also among the objects of this invention is to provide a two-stage process for the hydroforming of a hydrocarbon without the necessity for the employment of a higher pressure in the second stage.

50 Another object of the invention is a two-stage hydroforming process which does not require highly specific charging stocks.

55 A still further object of the invention is a two-

stage hydroforming process in which the catalysts have a longer activity period because coke formation has been reduced to a minimum.

Another of the several objects of this invention is to provide an improved hydroforming process which while it eliminates certain steps and features of prior art processes which are cumbersome, time consuming and expensive steps nevertheless retains and adds to the advantages thereof which have been derived.

Other objects and advantages are apparent from this specification, the appended claims and the drawing.

According to this invention there is provided a process for the hydroforming of a hydrocarbon in a specific manner which comprises the steps of passing said hydrocarbon into a catalytic conversion zone in which in a first section the hydrocarbon at a temperature in the range of 900–1100° F. is contacted with a chromia-alumina catalyst following which it is passed to a second section of said conversion zone directly without any intermediate steps wherein it is contacted at a temperature in the range 800–950° F. with a molybdenum oxide-alumina catalyst, the temperature in said second section always being lower than in said first section, to cause in the first section an optimum conversion for the chromia-alumina catalyst and in the second section an optimum conversion of the effluent of the first for the molybdenum oxide-alumina catalyst.

To more fully set forth and to describe the process of the invention reference is made to the drawing which diagrammatically illustrates the treatment of a hydrocarbon stream effected according to the invention.

A naphtha charge to be hydroformed is admixed with hydrogen and the mixture is preheated to a temperature of about 950–1100° F. and passed through conduit 1 into an adiabatic hydroforming zone 2 containing beds of chromia-alumina catalyst 3 supported on trays 4. The charge passes down through hydroformer 2 immediately passing over beds of molybdenum oxide-alumina catalyst 5 supported on trays 6 and then from the hydroformer through conduit 7. It is to be noted that the charge which has been contacted with the chromia-alumina catalyst, immediately and without any intermediate heating or separation step, is passed into contact with the molybdenum oxide-alumina catalyst. The desired time and extent of contact can be accomplished by suitable proportioning of the beds, their number and general configuration. While the hydroformer is illustrated to have uniform dimensions, it can be advantageously of diminishing cross-section or have less free space between each successive bed of catalyst in the line of flow to compensate for a diminished volume of hydrocarbon due to cooling thereof. Also the relative total quantity of the two catalysts, or hydrocarbon feed rate, can be varied readily for optimum results in case of each charging stock.

The chromia-alumina catalyst may also contain promoters or stabilizers; such as, beryllium and alkaline earth oxides. These catalysts may be prepared by any method known in the art. The molybdenum oxide-alumina catalyst may contain other promoters or stabilizers; such as, silica, alkali, alkaline earth oxides, vanadia, and tungsten oxide.

As stated, the temperature will be in the range 800°–1100° F. and that prevailing in the second section of the hydroformer will be lower than

that in the first section. Thus good results are obtainable when the temperature of the first section is about 950° F. to about 1050° F. and the temperature in the second section is about 930° F. to about 850° F. Optimum paraffin isomerization is obtained in the second section in this temperature range. Also, in general, the higher the temperature and the more paraffinic the naphtha used, the larger will be the ratio of chromia-alumina catalyst to molybdenum oxide-alumina catalyst. The molybdenum oxide-alumina catalyst will, in general, occupy 25–75% of the total catalyst space; for general use, about 50% is satisfactory. When the feed is a normal-paraffinic naphtha (low-octane number), the molybdenum oxide-alumina catalyst may be used in excess over the chromia-alumina. When the naphtha feed contains substantial amounts of isoparaffins (higher octane number), the chromia-alumina may predominate.

The chromia-alumina catalyst initially contains 5–45% Cr₂O₃, most of the remainder being Al₂O₃, and the use of 1–10% BeO or MgO being very desirable. The molybdenum oxide-alumina catalyst initially contains 5–30% MoO₃ deposited on alumina; 1–5% SiO₂ may also be present.

Feed rates of 0.5–2 volumes of naphtha per volume of catalyst per hour can be employed for satisfactory results.

The quantity of hydrogen can be about 500–5000 cubic feet per barrel of naphtha.

The pressure can be 50–500 pounds per square inch, preferably 200–250 pounds per square inch, for good results although pressures higher or even lower may be used.

The immediate treatment of the effluent of the first section in the second section tends to avoid substantially any reverse or even adverse reaction which can take place during a cooling, fractionation or separation and reheating steps as employed in the prior art.

The following example is illustrative of actual results obtained employing a tandem catalyst bed or hydroforming zone according to the process of the invention. Run B was on a more naphthenic naphtha than run A. The reactor vessel contained a chromia-beryllia-alumina catalyst in the upper half and a molybdenum oxide-silica-alumina in the lower half. Down-flow of feed was employed.

Example

Run.....	A		B	
55 Liquid Space Velocity, Vol./Catalyst Vol./Hr.....	Feed	1	Feed	1
Pressure, Lbs./Sq. In. Gauge.....	215		244	
Average Temperature, ° F.....	919		907	
Temperature Drop Through the Bed, ° F.....	950–861		951–848	
60 Product Yields, Wt. Percent of Naphtha Feed:				
C ₄ and Lighter Gases.....	10.0		10.1	
C ₅ + Hydrocarbon.....	86.7		87.4	
Coke.....	*0.5			
Loss.....	2.8		2.5	
65 Total.....	100.0		100.0	
Properties of C ₅ + Hydrocarbon:				
Research Octane Clear.....	22.7	66.7	64.5	88.5
Motor Octane Clear.....	28.2	62.2	64.8	78.4
Refractive Index (20° C.).....	1.4307	1.4400	1.4411	1.4580
Bromine Number.....	2.9	3.4	1.0	3.2

NOTES:

(1) The hydrogen to naphtha ratio was 2500 cubic feet per barrel.

(2) A five hour process cycle was employed.

(3) Most of the loss is believed to have been C₄ and lighter gases.

(*) The coke figure is slightly high due to shortness of run—5 hrs.

The increase in octane number as well as the

5

6

low percentage of coke are noteworthy in the example.

Reasonable variation and modification are possible within the scope of the foregoing disclosure and the appended claims to the invention the essence of which is that a considerably simplified two-stage hydroforming process which eliminates all the prior art cooling, fractionation, solvent extraction, reheating and pressure increasing steps and provides an optimum catalyst sequence wherein the entire charge is optionally converted in each zone with longer catalyst life (less coking) and therefore the saving of time and expense has been set forth and described.

I claim:

1. The hydroforming of a naphtha which comprises passing said naphtha at a temperature in the range 950°-1050° F. and a pressure in the range of 200 to 250 pounds per square inch gage into contact with a chromia-alumina catalyst in a first stage and then passing the effluent from said stage immediately and without any additional intermediate step directly into contact with a molybdenum oxide-alumina catalyst under hydroforming conditions in a second stage in which the temperature prevailing is lower than that in said first stage and is in the range 850°-930° F. and the pressure in said second stage is substantially the same as in said first stage.

2. The hydroforming of a naphtha which comprises passing said naphtha in admixture with hydrogen, and which admixture comprises the

sole feed to the process, at a temperature in the range 900°-1100° F. and a pressure in the range of 200 to 250 pounds per square inch gage into contact with a chromia-alumina catalyst in a first stage and then passing the effluent from said stage immediately and without any additional intermediate step directly into contact with molybdenum oxide-alumina catalyst under hydroforming conditions in a second stage in which the temperature prevailing is lower than in said first stage and is in the range 850°-930° F.; the pressure in said second stage being substantially the same as in the first said stage and withdrawing from second stage the sole effluent of the process.

ALFRED CLARK.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,955,297	Jennings	Apr. 17, 1934
2,293,759	Penisten	Aug. 25, 1942
2,322,622	Fischer et al.	June 22, 1943
2,345,575	Burk et al.	Apr. 4, 1944
2,348,624	Hillman	May 9, 1944
2,349,812	Day et al.	May 30, 1944
2,349,826	Layng	May 30, 1944
2,378,209	Fuller et al.	June 12, 1945
2,404,902	Claussen et al.	July 30, 1946
2,417,308	Lee	Mar. 11, 1947